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ANNUAL TECHNICAL REPORT
HIGH RESISTIVITY GaAs EPILAYERS BY OXYGEN DOPING

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6. AUTHOR(S)
M. Skowronski

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
CMU
5000 Forbes Ave.
Pittsburgh, PA 15213

8. PERFORMING ORGANIZATION REPORT NUMBER 152171

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
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13. ABSTRACT (Maximum 200 words)

During the first year of research our OMVPE system has been retrofitted with a charcoal exhaust scrubber, toxic gas detector, and process gas delivery system. All components have been fully tested and calibrated for GaAs deposition. High quality undoped GaAs epilayers have been deposited with following characteristics: specular morphology, low free carier concentration ($p = 1x10^{15}$ cm^{-3}) and high mobility (4,000 cm^2/Vs at 77K). The dominant acceptor is carbon originating from gallium source as detemined by the high resolution photoluminescence. Doping of GaAs epilayers with dimethylaluminum methoxide resulted in incorporation of both oxygen and aluminum in concentrations up to $5x10^{18}$ cm^{-3} and $7x10^{19}$ cm^{-3}, respectively. Oxygen concentration increases rapidly with decreasing deposition temperature. Heavily oxygen doped layers (obtained either by high DMAlMO flow or growth at temperatures below 600 °C) are highly resistive and exhibit exteremely low carrier lifetime. Photoluminescence measurements detected new luminescence bands in 850-1000 nm range which are assigned to deep oxygen induced traps.

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ANNUAL TECHNICAL REPORT

PROJECT TITLE:	High Resistivity Buffer Layers by Oxygen Doping
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This Annual Technical Report summarizes the research effort sponsored by AFOSR/NE for the period of September 1, 1991 to August 31, 1992. The original STATEMENT OF WORK is included as a Section 1 for the ease of comparison. This is followed by detailed description of technical accomplishments (Sections 2.1 through 2.4) brief summary of planned work, and list of publications and specific applications.

1. STATEMENT OF WORK

The goal of this project is to establish feasibility of growing high resistivity buffer layers of GaAs by oxygen doping. We intend to grow GaAs epilayers on n-type and semi-insulating GaAs substrates and dope them with aluminum and oxygen. The dopant source to be used is a novel compound: dimethylaluminum methoxide. Secondary Ion Mass Spectrometry will be used to determine the total oxygen and aluminum content and relate this to growth conditions. In particular, the effect of growth temperature on efficiency of oxygen and aluminum incorporation into GaAs will be investigated. The deposition temperature will be changed between 500 °C and 800 °C. The flow rate of DMAlMO will be correlated with concentration and type of point defects incorporated into GaAs layer. The primary characterization technique for defect assessment will be the localized vibrational mode absorption. Using ^{18}O isotope enriched DMAlMO will allow to determine the number of oxygen atoms involved in each defect and isotope shift due to naturally occuring ^{69}Ga and ^{71}Ga will be used to identify local symmetry of each center.

Two more technology related issues are the quality of overgrowth and thermal stability of electrical properties of buffer layers. Both the morphology of overgrowth and its electrical properties will be assessed. We plan to use Hall effect (electron concentration and mobility) to determine degree of compensation possibly caused by memory effect and photoluminescence to evaluate concentration of recombination centers. Thermal stability of electrical properties will be determined by Hall effect measurements before and after short (30 s) and long (2 hr) term annealing at typical processing temperatures.

2. STATUS OF RESEARCH EFFORT

2.1 Organometallic Vapor Phase Epitaxy System

During the initial part of the research period the effort has been focused on finishing the installation and testing of the Organometallic Vapor Phase Epitaxy system. The system itself has been purchased from Thomas Swan Ltd. but several critical components had to be either added or retrofitted. These included:

1) Activated charcoal exhaust scrubber has been designed, components have been purchased, assembled, and tested. The exhaust part of the OMVPE system is shown schematically in Fig.1. The scrubber and all tubing is made of stainless steel and its vacuum integrity is better than 10^{-9} Torr. In order to prolong the life of the charcoal charge and reduce toxic waste, the scrubber has been fitted with oxygen line for controlled oxidation of reaction products.

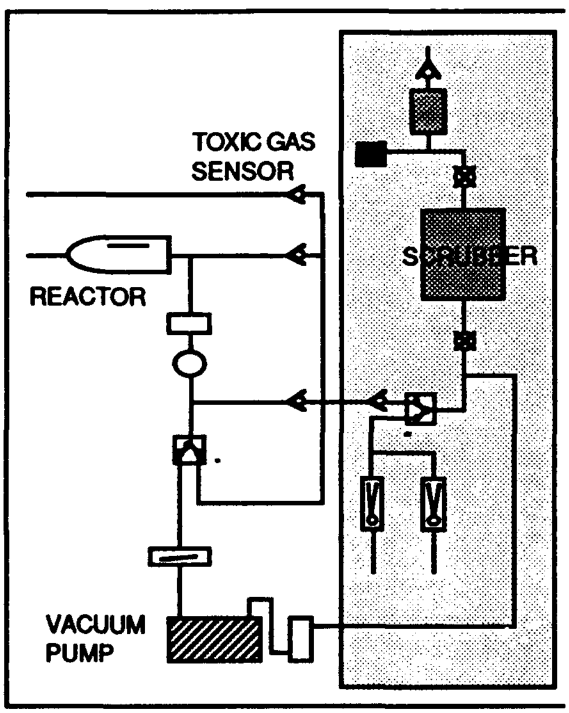

Fig. 1 Exhaust of OMVPE system (dotted area) designed and constructed at MSE.

2) Gas delivery systems for hydrogen and nitrogen process gases have designed, assembled and vacuum leak tested. For nitrogen we are using boil-off gas from GP-45 lN_2 tanks. Nitrogen tanks have to be replaced approximately once a month. Hydrogen is supplied from two banks of high pressure

cylinders each containing three cylinders. Both nitrogen and hydrogen lines are equipped with purge panels (donated by Bell Communication Research, Red Bank, NJ) and catalytic pre-purifiers.

3) Toxic gas detection system has been purchased using funds from ONR Grant, installed and tested.

4) Metalorganic sources have been purchased from American Cyanamide Co. (tertiarybutyl arsine) and Advanced Technology Materials (dimethylalumium methoxide). A gallium source (100 g of electronic grade trimethyl gallium) have been donated by AT&T, Holmdel, NJ. Sources have been installed and whole OMVPE system has been helium leak tested.

2.2 Growth and characterization of undoped GaAs.

In order to determine the effects of doping the properties of undoped layers had to be thoroughly characterized. We have investigated GaAs growth in the temperature range of 500 °C to 750 °C. The morphology of resulting layers have been determined by Nomarski contrast optical spectroscopy and specular surfaces have been obtained in the whole temperature range by adjusting the V/III ratio. The growth rate varied between 0.7 μm/hr to 2.0 μm/hr for optimized growth conditions and was controlled by the flow and decomposition of trimethylgallium. The decrease was observed only at low growth temperatures. The as-deposited undoped layers have been p-type with carrier concentration of 1×10^{15} cm^{-3} and hole mobility of 4,000 cm^2/Vs. This result indicates that layers are of very high quality. The p-type conduction is most likely due to incorporation of residual carbon of *trimethygallium*. The near band gap photoluminescence spectra are dominated by excitonic emissions showing well defined free exciton and excitons bound to neutral acceptors (Fig. 2). We have not observed excitons bound to neutral donors which indicates exceedingly low donor contamination.

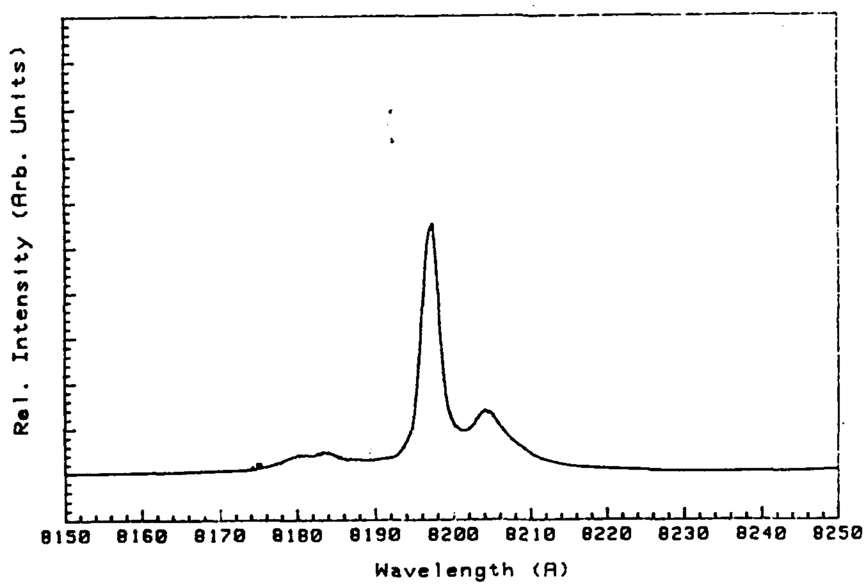

Fig. 2 High resolution photoluminescence spectrum of undoped GaAs epilayer grown at CMU.

2.3 Doping with dimethylaluminum methoxide

Doping of GaAs epilayers with dimethylaluminum methoxide was investigated in the 500 °C to 700 °C temperature range and 0.1 sccm up to10 sccm DMAlMO flow rate. For most of deposition conditions we have been able to obtain specular surface morphology. At the high doping level occasionally the surface was covered with small uniformly distributed features resulting in the hazy appearance of the layer. We have not observed any indications of gas phase reactions or change in dopant source over half a year time period. Dimethylaluminum methoxide appears to be stable "well behaved" metalorganic compounds.

The incorporation efficiency of aluminum and oxygen has been determined by Secondary Ion Mass Spectroscopy measurements performed by Charles Evans and Associates of Redwood City, CA. The aluminum content in epilayers does not depend on deposition temperature and is proportional to the DMAlMO flow rate. Oxygen incorporation, on the other hand, depends strongly on deposition conditions and increases rapidly with decreasing growth temperature. The typical epilayer structure used for SIMS analysis is shown in Fig. 3 while SIMS oxygen and aluminum profiles are presented in Fig. 3.

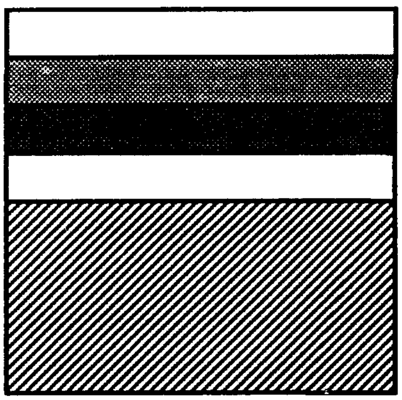

Fig. 3 Typical epitaxial structure used for Secondary Ion Mass Spectroscopy analysis.

The profile clearly shows that in DMAlMO doped material deposited at temperatures below 600 °C oxygen content exceeds 8×10^{16} cm^{-3} which is a SIMS detection limit in GaAs. The highest oxygen concentration achieved to date (with good surface morphology) is 5×10^{18} cm^{-3}. The width of the interfaces is smaller than 0.05 µm and is limited by the resolution of SIMS technique. There is no indication of memory effects in form of prolonged transients. Also, SIMS results prove that no significant oxygen interdiffusion occurs at growth temperatures.

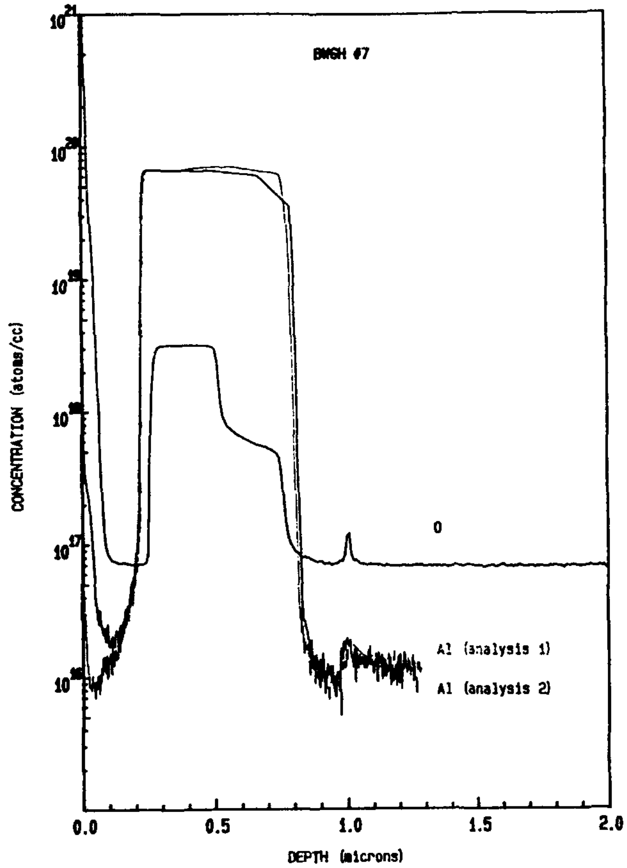

Fig. 4 SIMS profiles of oxygen and aluminum in structure shown in Fig.3.

2.4 Characterization of doped GaAs:Al-O layers

Several complementary characterization techniques have been used to assess effects of DMAlMO doping on properties of GaAs epilayers.

In photoluminescence experiments two important effects have been observed. In layers doped with DMAlMO the overall intensity of near band gap luminescence decreased significantly. In particular layers grown at low temperatures (600 °C and below) exhibited no detectable radiative recombination. This effect is apparently caused by deep levels associated with oxygen doping. Since the sensitivity of our system allows for detection of signals four orders of magnitude lower than luminescence from undoped epilayers and the carrier lifetime in good quality GaAs is no more than 10^{-8} seconds we can estimate that the carrier lifetime in our samples is no more than 10^{-12} s. Materials with such an extremely short carrier lifetime can be employed in ultrafast photodetectors.

In DMAIMO doped epilayers grown at higher temperatures the luminescence intensity is also lower as compared to undoped specimen but the difference is not as pronounced due to lower oxygen content. In these samples new luminescence bands appear in the 840 - 900 nm range (Fig. 5). Their intensities are correlated with DMAIMO flow rate and position indicates that they are due to deep levels within the band gap. The origin of the centers responsible for deep luminescence bands will be further investigated by Optically Detected Magnetic Resonance technique in cooperation with dr. T.A. Kennedy of Naval Research Laboratory.

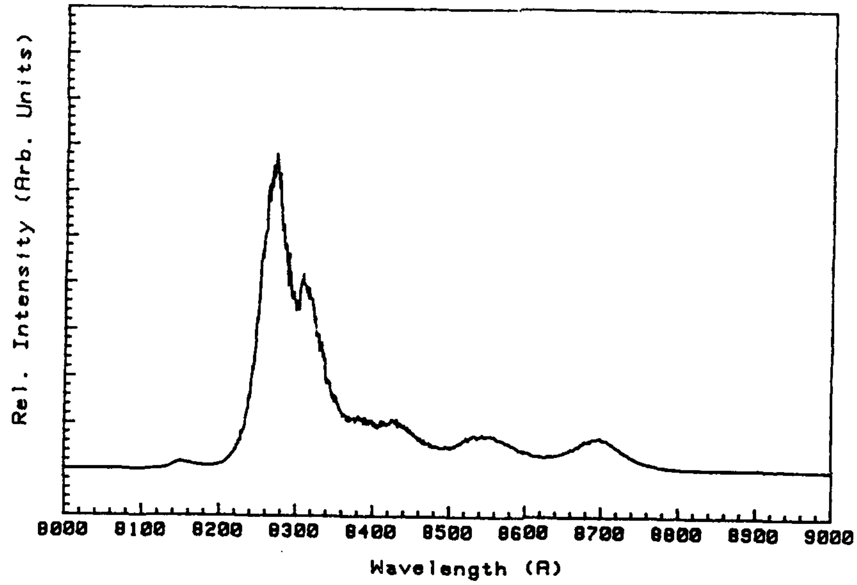

Fig. 5 High resolution photoluminescence spectra of GaAs epilayer doped with DMAIMO (Tg = 700 °C, f_{DMAIMO} = 2 sccm).

The electrical properties of doping have been assessed by Hall effect measurements at room and liquid nitrogen temperatures. The undoped layers were p-type with low (1×10^{15} cm^{-3}) hole concentration. The heavily doped samples were high resistivity and even for layer thickness of 3 μm fully depleted. It has been well established that oxygen acts as deep acceptor and can compensate shallow donors resulting in high resistivity material. Our measurements, however, provide the first experimental proof that oxygen also induces deep donors and can compensate p-type material. The position of compensating centers within the band gap will be determined in temperature dependent Hall measurements. The as-deposited epilayers have spent up to two hours at the growth temperature and can be considered as *in situ* annealed. Their high resistivity asserts the stability of electrical properties up to 600 °C. An independent series of post growth annealing experiments are underway. The initial annealing experiments at 800 °C for 30 minutes under arsenic overpressure resulted in decrease of resistivity. The layers turned p-type with hole concentration in the low 10^{16} cm^{-3} range. This effect could be caused by annealing out native defects induced by oxygen doping.

We have also made an effort to detect Localized Vibrational Modes of oxygen-related defects in doped epilayers in the 600 - 4000 cm^{-1} energy range. At present we are limited to this range because of the mercury-cadmium detector on our Bruker 113v FTIR spectrometer. The investigated spectral range, however, covers the energies of isolated oxygen vibrations in GaAs. Although the oxygen content exceeded detection limit by more than an order of magnitude no LVM lines were observed. This experiment conclusively proves that less than 10% of oxygen is present in the form of isolated centers and over 90% has to be present in the form of complexes with aluminum. In October 1992 a new infrared detector will be retrofitted into our FTIR and we will extend our measurements down to 200 cm^{-1}. This will allow for detection of substitutional oxygen bonding with aluminum.

2.5 Future work

There are three types of experiments planned for the next year.

1. Oxygen induced compensation in n-type GaAs.

As indicated above our undoped layers are invariably lightly p-type because of residual carbon from TMG. Our OMVPE system does not have a metalorganic line dedicated to n-type dopant and therefore up to now it was not possible to investigate the compensation of shallow donors. Since this is a critical part of the proposed work which can in industrial applications we plan to retrofit an additional metalorganic line into the deposition system. The n-type doping capability will make it possible to study acceptor levels of oxygen-aluminum complexes by temperature dependent Hall effect and by Deep Level Transient Spectroscopy. Both experimental techniques have been proposed as means of characterization in the original research plan.

2. Thermal stability and oxygen outdifusion.

Because of the technological importance we will focus on effect of annealing and thermal stability in compensated n-type layers. We are planning to perform Rapid Thermal Annealing using halogen lamp heating in face-to-face configuration and long term annealing (30 minutes to 1 hour) in conventional furnace under arsenic overpressure. Annealed epilayers will be characterized by Hall effect to assess changes in resistivity, optical absorption to monitor nature of centers, DLTS for defect concentration, and SIMS to measure diffusion coefficient.

3. Overgrowth morphology and properties.

The DMAlMO doping is intended for growing high resistivity buffer layers for device isolation. It is, therefore, crucial for the success of the project to investigate the quality of the active n-type layers deposited on top of the buffer. The cross-contamination between layers and presence of oxygen-related traps in channel of GaAs MESFET will result in degradation of device performance. The donor doped active layers will be deposited on top of the buffer and their quality assessed by photoluminescence, Hall effect and DLTS.

PUBLICATIONS AND CONFERENCES

1. "Complexes of oxygen and native defects in GaAs", M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, accepted to Physical Review B, scheduled for publication in November 1992.
2. "Alkoxide doping of GaAs during OrganoMetallic Vapor Phase Epitaxy", Y. Park and M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, accepted for presentation at Materials Research Society 1992 Fall Meeting, Boston, November 1992.

planned:

3. "Oxygen and aluminum incorporation into GaAs epilayer by dimethylaluminum methoxide doping during metalorganic chemical vapor deposition" Y. Park and M. Skowronski, Department of Materials Science and Engineering, Carnegie Mellon University, T. Ruseel, Oak Ridge National Laboratory.

The joint research effort was planned for the summer of 1992 with dr. Omar Manasreh of Solid State Electronics Division (WL/ELRA) , Wright Patterson Air Force Base. Because of the change in research thrust in ELRA group this project could not be finalized. However, we are planning to cooperate with drs. W.C. Mitchel and D. Fischer of WL/MLPO on defects characterization. It is anticipated that a seminar will be presented at WPAFB in early 1993.

INVENTIONS, PATENT DISCLOSURES AND APPLICATIONS

The driving force behind this project is the potential application of DMAIMO doped GaAs in electronic devices. It has been hoped that heavily doped layers will be suitable for the high resistivity buffers layers in GaAs technology. Preliminary growth and characterization results demonstrate that indeed this approach appears feasible and several other applications are possible as well. They are briefly summarized below.

2.1 High resistivity buffer layers for reduction of side- and back-gating in GaAs integrated circuits.

A number of problems associated with GaAs MESFET devices and circuits are attributed to the semi-insulating substrate. These include side- and back-gating and low source-drain breakdown voltage. In order to reduce the flow of current in high resistivity substrate its is important to increase the concentration of compensating centers and as a consequence increase the so-called trap-filled-limit voltage.[1] A device isolation scheme employing the high resistivity buffer is sketched on Fig. 6.

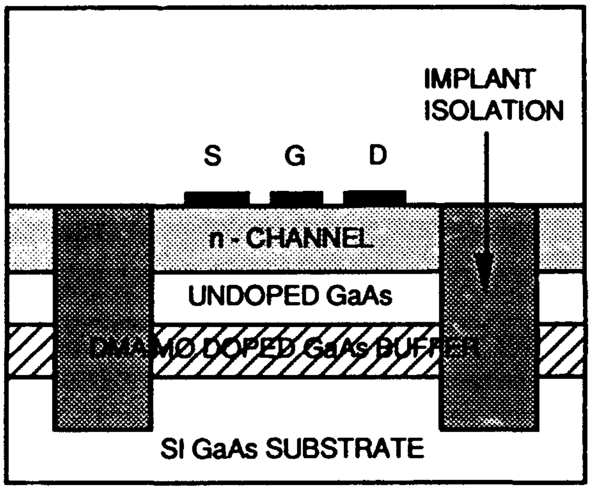

Fig.6 GaAs MESFET structure employing high resistivity buffer for backgating reduction.

2. Compensation of conducting epilayers.

Another potential application of Al-O doping could be the compensation of the conducting interfacial layer of GaAs deposited on silicon substrates.[2] The GaAs/Si interface contains high density of point and extended defects due to the lattice mismatch which promotes the diffusion of silicon into GaAs epilayer. The SIMS data indicate the Si content as high as 10^{19}-10^{20} cm^{-3} in the interfacial region with free electron concentration in the 10^{18}-10^{19} cm^{-3} range. This highly conducting layer causes parasitic capacitances in the MESFET structures and degrades device performance at high frequencies.[3] It has been suggested that implantation induced damage could be used in order to compensate the silicon donors.[2] This approach has been later realized in practice.[3] After deposition of a thin buffer GaAs layer, growth was interrupted and the structure implanted with H^+. This was followed by the deposition of n-type active layers. Using DMAlMO doping it should be possible to compensate the interfacial layer without taking the wafer out of the growth system significantly simplifying the processing. Since the Al-O complex has a high solid solubility and induces both deep acceptor and donor levels, the compensation should not depend sensitively on the DMAlMO flow. It is expected that this doping scheme would yield a high resistivity buffer even for highly nonuniform silicon distribution in the layer.

3. Surface layers for GaAs MESFETs and M-S-M photodetectors.

Another serious problem in GaAs technology is the high field surface conductivity between device terminals. The highest electric field is usually present between gate and drain and MESFET performance is frequently limited by low gate-drain breakdown voltage. The surface conductivity leading to breakdown is in fact analogous to side-gating effects in bulk wafers. The concentration of deep compensating centers close to the surface is sometimes reduced due to out diffusion and stoichiometry changes during processing. This in turn lowers the surface layer V_{TFL}. It has been demonstrated experimentally that employing surface layer with high deep center density (such as LT MBE GaAs and Al-O doped GaAs) significantly increases the breakdown voltage (Fig. 6).

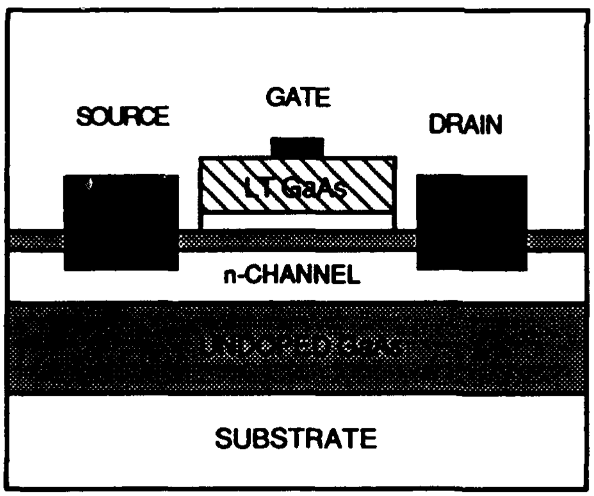

Fig. 7 Material with high deep trap density significantly increases the gate-drain breakdown voltage (after Yin *et al.*[4]).

A similar function Al-O doped layer can fulfil in Metal-Semiconductor-Metal (MSM) detectors. MSM photodetectors are very attractive for optical communication systems, high-speed chip-to-chip connection, and high speed sampling. A high speed of operation can be achieved by using material with ultrashort carrier lifetime. Devices from the first group utilized high defect density materials such as oxygen-implanted silicon on sapphire,[5] He^+ implanted InP,[6] and low temperature MBE GaAs.[7,8] Since Al-O doped GaAs exhibits extremely short carrier lifetime (see above) it also should be suitable for this application. The potential advantage of GaAs:Al-O over that of other materials is the controlled deep level density. It does allow for optimization of electron mobility - electron recombination rate product.

The above application have not yet been directly demonstrated in practice because of the modest amount of funding and relatively short time. According to preliminary experimental results, however, all of the above appear feasible.

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